DECORATING WITH EXPLOSIVES: THE USE OF *AURUM FULMINANS* AS A PURPLE PIGMENT

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Supplemental Material

Introduction

The polychrome decoration of terracotta and glazed earthenware using metal oxides was already known since early antiquity, and the decoration of porcelain with overglaze enamels had begun in China during the early Ming Dynasty (1368-1644). A full palette of colors including red, green, yellow, turquoise, violet and black had been developed and was in widespread use by the Chenghua era (1464-1487).

The Meissen Manufactory, despite its initial success as Europe's first hard-paste- porcelain manufactory, had substantial difficulties with overglaze polychrome decoration during the first decade of its existence (1). In his famous Memorandum to the King, of March 28, 1709, Johann Friedrich Böttger (1682-1719) had promised, among other technical advances, the production of "the good white porcelain with the finest of glazes and all the proper painting…" (2). Despite some crude steps taken in that direction (3), the promise of "all the proper painting" was never fully realized during Böttger's lifetime. The Manufactory Commission often expressed its displeasure over the state of the art. So it was with great pride and considerable relief that Manufactory Inspector (4) Johann Melchior Steinbrück (1673-1723) could announce in his 1717 report on the state of the Manufactory the invention of a decorating technique for porcelain (5):

> Therefore one should not doubt that one will gradually discover whatever is still missing [in technology] and introduce it. Just as a short while ago a truly new way of decorating called Mother-of-Pearl or Opal glaze (even though it of course is not a glaze) was applied onto white porcelain, to which it imparts a new and very beautiful appearance.

This new decoration gave the white surface of porcelain a pink to violet lustrous tint with a sometimes mottled and cloudy appearance and later came to be known as Böttger luster. Only a handful of objects from the Böttger period (1710-1719) decorated in this fashion exist today, six (three cups and their associated saucers) are on display at the State Porcelain Collections in Dresden and a cup and saucer are kept in storage at the Metropolitan Museum of Art in New York City. In a subsequent memorandum written in 1719 Steinbrück provides a little more background about the invention (6):

> …the Mother-of-Pearl glaze also stems from Böttger, and he taught it to Mehlhorn and Funcke and allowed them to experiment at his expense (as the glaze is made of gold)…

We are told for the first time that gold is a main ingredient of this new decoration. Also, in Steinbrück's view Böttger was the inventor, though he also mentions Böttger's coworker Johann George Mehlhorn and acknowledges the participation of George Funcke. Funcke was listed as master goldsmith and enameller in the Dresden municipal archives (*Ratsarchiv*) from 1692 until 1726. He joined Böttger's circle of close coworkers in 1710 and was listed as a Meissen employee until May 1713. During this time he was involved in the gilding and early enamel decoration of Böttger porcelain with a rather limited palette of colors. Thereafter he worked as an independent contractor paid piecemeal for his decorative work. Given Böttger's inability to develop reliable polychrome decoration in house, the Manufactory management began viewing reliance on an outside contractor with considerable trepidation. Following Steinbrück's concerns about the confidentiality of trade secrets, Funcke was forced to enter an exclusive contract with Meissen, involving eight types of decoration, encompassing pretty much everything that Meissen offered for sale. Number eight on the list was decoration with mother-of-pearl glaze (Böttger luster) (7).

Our knowledge of Funcke's work comes mainly from periodic memoranda filed by Steinbrück who was also Böttger's brother-in-law and whom he served with great loyalty and devotion. In these memoranda, Funcke is consistently depicted merely as a competent technician following Böttger's instructions. But Funcke was also an accomplished goldsmith with experience in the enameling of gold and silver. Many scholars have therefore suggested that Funcke has not received sufficient credit for his contributions to the development of porcelain decoration. The chemical origins of the "Böttger luster" discussed in this paper will point to a more pivotal role for Funcke in the invention of this decorative technique.

No explicit recipes for Böttger luster dating to the actual Böttger period are known today. The earliest known formal documentation of this process had to await the arrival of that most celebrated porcelain painter of all, Johann Gregorius Höroldt.

The Arrival of Johann Gregorius Höroldt

Böttger died on March 13, 1719, after a protracted illness. In anticipation of Böttger's imminent death Augustus (at that time King of Poland as well as Prince Elector of Saxony) had made arrangements to salvage as much of Böttger's library of books, laboratory notebooks, manufactory-related business documents as possible and any samples of experimental ceramic materials (8). Böttger was under oath to document his research and according to his closest associates kept detailed notes of his work. Nevertheless, no documents describing his experiments after 1708 are known to exist today.

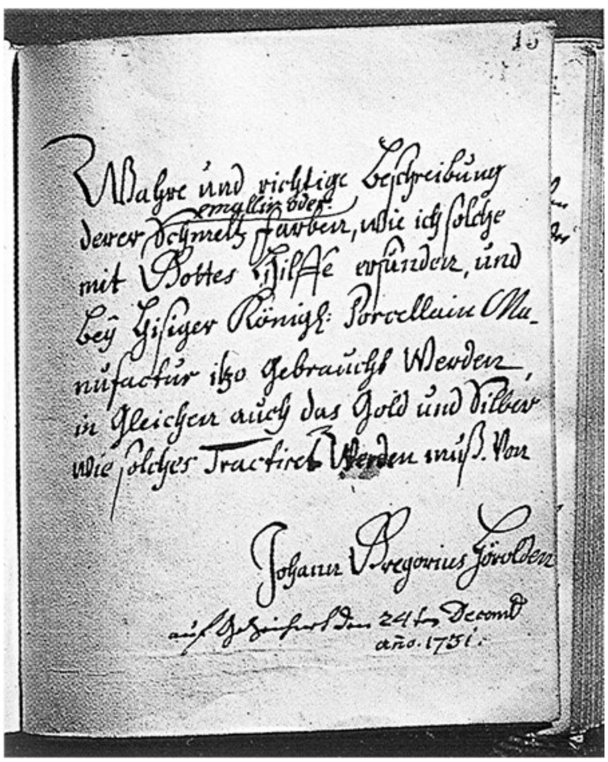
During the rest of 1719 the Manufactory Commission tried to secure the continuation of the business. Part of that was to protect intellectual property against the incursions of the emerging competition in Vienna. Samuel Stöltzel (1685-1737), one of Böttger's closest associates, and in possession of the *Arcanum*, (the closely guarded secret formula for making porcelain), had defected to the newly founded Vienna Manufactory of Claudius Innocentius du Paquier just two months prior to Böttger's death. Stöltzel's betrayal of the *Arcanum* accelerated the emergence of a second, competing porcelain manufactory in Europe. Fearful of losing its position of monopoly, on June 17, 1719, Meissen signed a contract with Funcke stipulating that he could not sell privately Meissen porcelain decorated in his shop (9).

According to the Saxon State Archives, Funcke was on record as having expertise in the painting of porcelain with the colors black, green, purple, deep purple, blue and red, by employing the same techniques he applied to the enameling on gold and silver (10). Funcke had perfected the techniques of gilding porcelain and stoneware. In contrast, the quality of Funcke's overglaze enamels on porcelain lacked the crispness and vibrancy of color the Meissen Manufactory was destined to achieve within less than a decade after Böttger's death. The turning point came with the arrival of Johann Gregorius Höroldt (1696-1775) on May 16, 1720, a pivotal event that forever changed Meissen's fortunes.

Little is known about Höroldt's early life, prior to his joining the Meissen Manufactory. He was born in Jena in 1696 as the son of a tailor and was probably trained as a draftsman, engraver, or enameller. It is known that in 1718 he was working as a carpet painter in Strasbourg and moved that year to Vienna to continue in the same line of work. Once in Vienna, he quickly established contact with the newly founded Du Paquier Manufactory, probably through the intermediation of Christoph Hunger, an earlier Meissen defector. It was there that Höroldt met and befriended Stöltzel. When a disillusioned Stöltzel decided to return to Meissen, he brought Höroldt with him as some sort of a trophy to mollify the powers that be since defection from Meissen was a serious offense. Höroldt was introduced simply as "an established and well-trained artistic painter."

Thanks to his diligence and artistic talents, within a few years Höroldt became the undisputed leader in the area of porcelain decoration. Nevertheless, as far as the preparation of pigments is concerned he initially depended almost entirely on Stöltzel and David Köhler (1683-1723), another of Böttger's associates (11). One could hardly expect Höroldt to immediately distinguish himself in pigment technology. Within a decade, however, he was able to integrate the disparate knowledge of individual arcanists into a coherent whole, thus generating an adequately broad palette of colors. Progress did not come easily since Höroldt did not have a workplace within the Manufactory until 1722.

Initially Höroldt worked as an independent contractor with his own staff of painters and was paid by the piece. A series of embezzlements and shady deals under Meissen Manufactory director Carl Heinrich Graf von Hoym were uncovered at the beginning of April 1731. This event led to the demand by the Manufactory Commission to document the intellectual property of the manufactory. On April 12, four leather-bound notebooks with parchment pages were distributed to key people, namely, Samuel Stöltzel, Johann Andreas Hoppe, Johann Georg Schubert and Höroldt to write down "*sämtliche Wissenschaften*", i.e. their entire knowledge of the manufacturing process. Stöltzel, Hoppe and Schubert had their documentation completed by May 1 of that year. Höroldt did not start writing until Christmas of that year.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Wahre und richtige Beschreibung
derer emaillir oder Schmeltz Farben, wie ich solche
mit Gottes Hülffe erfunden, und
bey hiesiger Königl: Porcellain Ma-
nufactur itzo gebraucht werden,
in gleichen auch das Gold und Silber
wie solches Tractiret werden muß. Von

Johann Gregorius Höroldt
[illegible] den 24ten Decemb
año. 1731.

Figure 1. *Cover page of Höroldt's book of recipes. The full title is "True and correct description of the enamel or melt colorants that I have invented with the help of God and which are in use in this the Royal Porcelain Manufactory and also the Gold and Silver and how they should be treated, Johann Gregorius Höroldt, entered on the 24th of December of the year 1731"*

An overview of the Höroldt recipes from a technological point of view has been published by Seyyfarth (12) and in somewhat more detail by Mields (13). Neither paper gives complete transcripts of the procedures. Höroldt's handwritten book consists of 19 chapters on color and flux recipes, and one chapter on ovens and the firing of painted porcelain (14).

The front page of Höroldt's book of recipes is shown in Figure 1. The text is always on the right side of the notebook. The left side is reserved for notes and clarifications. The chemical operations and processes employed by Höroldt give us a unique insight into the laboratory practices of the period. They can be summarized as follows:

1. All starting materials were first calcined at a temperature corresponding to the bisque firing step in the production of porcelain (a temperature scale expressed in degrees was unknown at the time, the actual temperature range for bisque firing is thought to have been 900-1000 °C).

2. Mechanical processing (grinding) of the raw materials included quenching from high temperatures for the initial break-up of the ores (for example quartz) as delivered, coarse grinding in iron or brass mortars (with consideration given to which mortar material would introduce the least amount of interfering impurities), separation of particles by size using sieves made of hair, and further grinding. Flotation was also used as an alternative method for the separation of particles by size. Agate mortars were used for fine grinding. Compounding of the powdered ingredients was carried out in dry form.

3. Chemical processing included roasting, decomposition using alkalis or acids, and precipitation. The filtering of precipitates was known, but seldom used; decantation was instead the method of choice. Sand baths were used for mild heating and solvent removal.

4. Oxidation of metals and alloys like Cu, Pb, Sn, and brass by heating them in air (converting them into what was termed metal ash followed procedures developed previously by potters. The health hazards of vapors released in some of these processes were pointed out.

Höroldt's Recipe for Böttger Luster and its Origins in Alchemy and Early 17th Century Chemistry

Chapter 11 on "How the Mother-of-Pearl or Copper Color is Made" (Figure 2) is the first and only known detailed recipe for Böttger luster. The recipe is six pages long (odd numbered pages 111-121) plus one page (120) containing a brief footnote. We have transcribed and translated the entire chapter. Facsimiles of the handwritten pages, and a modern German transcript and English translation by the author are available as Supplemental Material on the *Bulletin* website. An outline of the recipe is given below:


111
Das XI. Cap:
Wie die Perllmutter oder Kupffer farbe gemacht wird.

Figure 2. *Facsimile of the first page of chapter 11 from Höroldt's book of recipes, describing the preparation of the mother-of-pearl or copper color (i.e. Böttger luster). A complete transcript of the text and English translation of the chapter are available as Supplemental Material.*

1. Bring a gold ducat to red heat, cut it and dissolve it in aqua regia.

2. Neutralize the solution by slowly adding *oleum tartari* (concentrated aqueous potassium carbonate) until bubble formation stops and let it stand for a day and dilute it with a pot of hot water.

3. Decant the supernatant and heat to almost dryness

4. A warning is given against the explosive nature of the thoroughly dried precipitate that can lead to injury.

5. Mix the yellow precipitate 2:1 with lead silicate flux in an agate mortar; to paint apply it as thinly as possible.

6. Prepare *oleum tartari* by calcination of potassium tartrate and dissolve it in the least amount of water possible, remove the insoluble impurities using a filter made of blotting paper.

The footnote on page 120 explains the reasons for preheating the gold coin: "Easier to cut and dissolves faster."

Upon reading the above a chemist should immediately ask the question: "How can this procedure lead to an explosive compound?" The answer to this question can be found in the earliest reported recipe for this material as it appears in the work of the alchemist(s) who wrote under the pseudonym Basil Valentine.

The author of the Valentine corpus represents himself as a Benedictine monk from Rhineland. The first five books, ostensibly by Basil Valentine, were published by Johann Thölde (1565-ca.1614). Thölde was a chemist, part-owner of the salt mines in Frankenhausen am Kyffhäuser (Thuringia), and member of the city's Chamber of Councilors (Rathskämmerer). He claimed to be in possession of the original Valentine manuscripts. No evidence for a person by the name of Basil Valentine exists prior to the publication of the manuscripts by Thölde who probably is the real author of most of the content. The books were written no earlier than 1590 and reflect the ideas of Paracelsus. Thölde also published the work on antimony of another Paracelcist, Alexander von Suchten (1520-1575). A thorough refutation of both the existence of a 15th century monk by the name of Basil Valentine and of the early date for the Valentine corpus claimed by Thölde (which, if true, would have predated the work of Paracelsus (1493-1541)) was given by Stillman (15). More recently, Principe (16) has given an extensive analysis of the Valentine corpus in *The Secrets of Alchemy*. A particular point brought up by Principe is Valentine's attempt at detoxification of antimony by using the Paracelsian principle of *Scheidung* (meaning separation of properties rather than components), a point to which we shall return shortly.

In his longest book, *The Last Will and Testament*, Valentine gives a recipe for an explosive gold compound. A facsimile of the passage describing the preparation of this explosive "gold calx" (*Goldkalck* in the original German text) taken from the first English edition of the book (17) is reproduced in Figure 3. The Valentine procedure, outline below, is essentially identical to Höroldt's recipe for Böttger luster, which it predates by at least a century, *with one key piece of information in the first step not mentioned by Höroldt*.

1. Prepare aqua regia by dissolving 8 lot (4 ounces) of *sal armoniac* (ammonium chloride) in one pound of good strong *aqua fortis* (nitric acid).

2. Dissolve thin gold foils in aqua regia.

3. Neutralize solution with concentrated potassium carbonate

4. Wash precipitate up to twelve times with water followed by decantation.

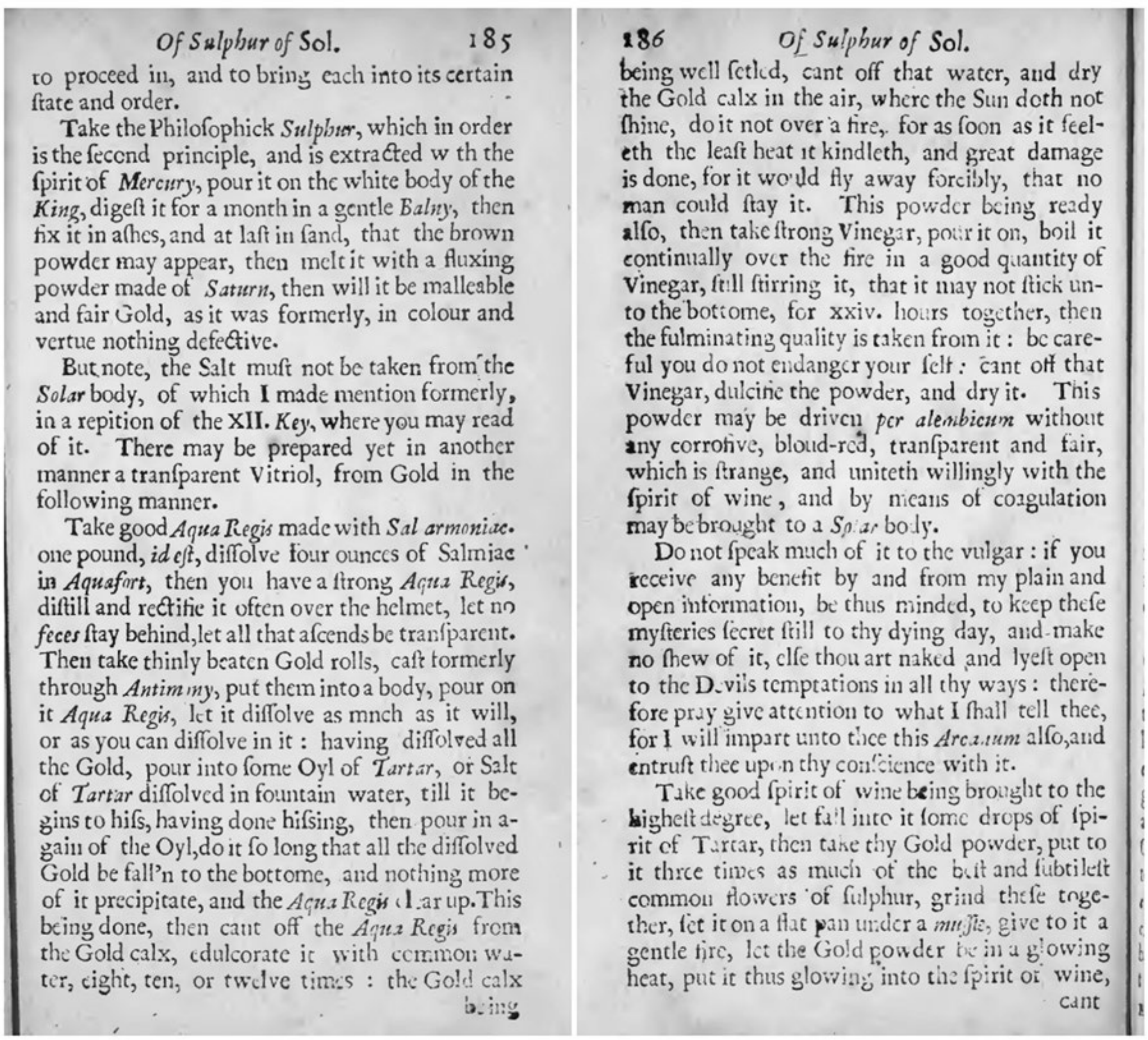
5. Decant the supernatant and allow the precipitate to dry but not over fire.

6. Warning that the least amount of heat ignites the powder leading to great damage.

7. Its fulminating quality can be removed by boiling it in strong vinegar for 24 hours, "dulcifying" it i.e. diluting it with water (presumably until the taste is no longer objectionable) and drying it. The blood red powder can be driven *per alembicum* and can be converted to gold by means of coagulation.

In step one we learn that Valentine makes aqua regia by using a mixture of nitric acid and ammonium chloride, not hydrochloric acid (as modern chemists would do), a point about which Höroldt is silent. Actually this formulation for aqua regia using ammonium chloride is given already by Georgius Agricola (1494-1555) in *De Re Metallica* (18). As we shall see in the next section the presence of ammonium ions is essential to the formation of this explosive precipitate.

The naming of this material during the first quarter of the 17th century was still in flux. In his *Tyrocinium Chymicum* (first published in 1610) iatrochemist Jean



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to proceed in, and to bring each into its certain ſtate and order.

Take the Philoſophick *Sulphur*, which in order is the ſecond principle, and is extracted w th the ſpirit of *Mercury*, pour it on the white body of the *King*, digeſt it for a month in a gentle *Balny*, then fix it in aſhes, and at laſt in ſand, that the brown powder may appear, then melt it with a fluxing powder made of *Saturn*, then will it be malleable and fair Gold, as it was formerly, in colour and vertue nothing defective.

But note, the Salt muſt not be taken from the *Solar* body, of which I made mention formerly, in a repition of the XII. *Key*, where you may read of it. There may be prepared yet in another manner a tranſparent Vitriol, from Gold in the following manner.

Take good *Aqua Regis* made with *Sal armoniac*. one pound, *id eſt*, diſſolve four ounces of Salmiac in *Aquafort*, then you have a ſtrong *Aqua Regis*, diſtill and rectifie it often over the helmet, let no *feces* ſtay behind, let all that aſcends be tranſparent. Then take thinly beaten Gold rolls, caſt formerly through *Antimony*, put them into a body, pour on it *Aqua Regis*, let it diſſolve as mnch as it will, or as you can diſſolve in it : having diſſolved all the Gold, pour into ſome Oyl of *Tartar*, or Salt of *Tartar* diſſolved in fountain water, till it begins to hiſs, having done hiſsing, then pour in again of the Oyl, do it ſo long that all the diſſolved Gold be fall'n to the bottome, and nothing more of it precipitate, and the *Aqua Regis* clear up. This being done, then cant off the *Aqua Regis* from the Gold calx, edulcorate it with common water, eight, ten, or twelve times : the Gold calx being

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being well ſetled, cant off that water, and dry the Gold calx in the air, where the Sun doth not ſhine, do it not over a fire, for as ſoon as it feeleth the leaſt heat it kindleth, and great damage is done, for it would fly away forcibly, that no man could ſtay it. This powder being ready alſo, then take ſtrong Vinegar, pour it on, boil it continually over the fire in a good quantity of Vinegar, ſtill ſtirring it, that it may not ſtick unto the bottome, for xxiv. hours together, then the fulminating quality is taken from it : be careful you do not endanger your ſelf : cant off that Vinegar, dulcifie the powder, and dry it. This powder may be driven *per alembicum* without any corroſive, bloud-red, tranſparent and fair, which is ſtrange, and uniteth willingly with the ſpirit of wine, and by means of coagulation may be brought to a *Solar* body.

Do not ſpeak much of it to the vulgar : if you receive any benefit by and from my plain and open information, be thus minded, to keep theſe myſteries ſecret ſtill to thy dying day, and make no ſhew of it, elſe thou art naked and lyeſt open to the Devils temptations in all thy ways : therefore pray give attention to what I ſhall tell thee, for I will impart unto thee this *Arcanum* alſo, and entruſt thee upon thy conſcience with it.

Take good ſpirit of wine being brought to the higheſt degree, let fall into it ſome drops of ſpirit of Tartar, then take thy Gold powder, put to it three times as much of the beſt and ſubtileſt common flowers of ſulphur, grind theſe together, ſet it on a flat pan under a *muffle*, give to it a gentle fire, let the Gold powder be in a glowing heat, put it thus glowing into the ſpirit of wine, cant

Figure 3. *Passage describing Valentine's procedure for making gold calx (later known as aurum fulminans) taken from Ref. 17.*

Beguin (1550–1620) gives a recipe identical to that of Basil Valentine (19). A footnote on p. 293 of the 6th edition that appeared in 1625 states: "The Germans say *das Schlaggoldt*, in Latin [it is called] *aurum fulminans* because it gives forth a very sharp sound like thunder as it explodes. [Oswald] Kroll calls it *aurum volatile*" (20). To complicate matters further, in the text itself Beguin uses the term "Ceraunochryson" derived from the Greek keraunos (thunderbolt) and cruson (golden). Also in the German literature after the middle of the 19th century one typically encounters the word "*Knallgold*." At the present time, however, the term used most commonly is *aurum fulminans* and that is what we shall use throughout the remainder of this paper.

What is *Aurum Fulminans*?

At this point a brief review of the chemistry of *aurum fulminans* would be useful for the purposes of the subsequent discussion. The name *aurum fulminans* and the shock-sensitive nature of this material might lead one to believe that it is simply gold fulminate (AuCNO) a salt of fulminic acid (HCNO). This is definitely not the case. The reaction of gold with aqua regia yields $AuCl_3$. In neutral to slightly alkaline media mild reducing agents convert Au(III) to Au(I). The formation of AuOH from Au(III) and hydrogen sulfite ion, for example, is a well-known reaction (21).

$$Au^{3+} + HSO_3^- + 2H_2O \rightarrow$$
$$HSO_4^- + 3H^+ + AuOH \text{ (dark violet precipitate)}$$

Ammonia can also act as a mild reducing agent and when reacted with Au^{3+} yields the highly explosive compound gold(I) hydrazide which indeed is *aurum fulminans*.

$$Au^{3+} + 2NH_3 \rightarrow AuNHNH_2 + 3H^+$$

It should now be evident why aqua regia prepared in the historical manner is so important to the success of this synthesis. Already during the early 17th century several authors pointed out that using sodium chloride rather than ammonium chloride as the source of chloride ions in aqua regia does not lead to an explosive product. In fact Rudolf Glauber (1604-1670) observes that using *spiritus urinae* (probably ammonium carbonate) instead of *oleum tartari* for the neutralization/precipitation step leads to a better explosive (22) (presumably by improving the reaction yield).

The detoxification of antimony discussed by Principe and mentioned in the previous section is not the only instance when Valentine entertains the possibility of selectively removing an undesirable property from a material. Valentine describes how heating *aurum fulminans* in vinegar under constant stirring for 24 hours (!) yields a "bloud-red" product that is not explosive. This product can be converted to gold through the process of "coagulation." We have not performed actual replication experiments as part of our research. We speculate that the "removal" of the fulminating property observed by Valentine involves decomposition of gold hydrazide. The "bloud red" color could be caused by finely divided gold in suspension or, if an iron implement was used for stirring, it could be due to the formation of iron acetate as in the case of antimony. While the removal of the undesirable fulminating property through chemical means is illusory, surprisingly the suppression of uncontrolled fulminations by physical means proved feasible, as we shall see in the next section.

The Use of *Aurum Fulminans* in the Decorative Arts

Aurum fulminans is a highly unstable compound that is recorded on numerous occasions as having caused substantial physical damage and even a few casualties. Could such a material have found any use in the decorative arts of the 17th and 18th centuries, particularly in a manufactory setting such as Meissen? In this section we shall present archival evidence showing that *aurum fulminans* was indeed commonly used by jewelers and enamelers long before the time of Höroldt and Böttger, and conclude by reexamining the role of the goldsmith Georg Funcke in the invention of Böttger luster.

The purple color or lustrous coppery tone of Böttger luster should not be confused with another gold-based deep-red to purple colorant known as the Purple of Cassius, though both owe their color to the formation of metallic gold nanoparticles. In the case of the Purple of Cassius, the nanoparticles are precipitated by the addition of stannous chloride to $AuCl_3$ and are stabilized by the colloidal hydrated SnO_2 ("stannic acid") produced during the redox reaction. The Purple of Cassius was well known, widely used in the production of ruby glass and as enamel color on ceramics and is still in use today. Its colloidal nature was determined by Richard Zsigmondy (1865-1929). The study became part of the body of work for which Zsigmondy was awarded the 1925 Nobel Prize in Chemistry. An excellent review of the history of the

Purple of Cassius was published by Hunt (23). The preparation of the Purple of Cassius and its application to porcelain painting are described separately, in chapter 10 of Höroldt's book of recipes (14). *By contrast, no Sn is detected in Böttger luster by X-ray fluorescence* (24). As we shall see, the finely divided gold is produced by the thermal decomposition of *aurum fulminans*.

The earliest detailed account of the physical and chemical properties of *aurum fulminans* was given by Torbern Bergman (1735-1784) in his *Opuscula Physica et Chemica* first published in 1780. Bergman was professor of chemistry and mineralogy at the University of Uppsala, a member of the Royal Swedish Academy of Sciences and Fellow of the Royal Society of London. He was a proponent of the phlogiston theory and a follower of Johann Joachim Becher (1635-1682/85) and Georg Ernst Stahl (1660-1734). The *Opuscula* (Essays) comprise six volumes and are a collection of Bergman's scientific papers and memoirs. Dissertation XVII (25) titled "Of the Fulminating Calx of Gold" describes

> …experiments, which are partly new, and partly such as have been described by others but carefully revised and corrected…

In the opening paragraph of the first section Bergman informs us that he undertakes the study of this material in the belief that an understanding of the various phenomena associated with its explosive nature:

> **Historical Introduction**
>
> Although the wonderful fulminating property of gold was known at least in the 15th century, it has not been yet examined by the philosophers so as to determine the cause of the prodigious noise and stupendous explosive force; yet in this explosion there occur phænomena highly worthy of attention-phænomena whixh not only indicate very singular properties, but are of such a kind that the causes of them, well understood, must certainly throw great light upon the theory of chemistry.

Dissertation XVII consists of 14 sections, and an in-depth critique of the rather lengthy essay is outside the scope of the present paper (26). Bergman does make several observations relevant to our topic, and we shall restrict our discussion to these salient points.

In the *Historical Introduction* Bergman recognizes Basil Valentine as the "perhaps first who has clearly described the method of communicating this property to gold" though the opening paragraph implies that he has fallen for Thölde's hoax of an early 15th century authorship. Quite telling are his quotes of Georg Ernst Stahl (1660-1734) and Robert Dossie (1717-1777):

> The celebrated Stahl says, that *aurum fulminans*, treated with sulphur, as hereafter described, *is used as a pigment by goldsmiths and enamellers* [emphasis added by the author]. Dossie mentions this as a valuable secret.

Here we have a significant first clue to the use of this material as a pigment. A further clue as to how *aurum fulminans* might have been handled safely comes in section IV titled "*Means by which the fulminating property may be destroyed*":

> …by the addition of a dry substance of any sort provided it be well pulverized, and intimately mixed with the *aurum fulminans* by trituration, so that the particles of the latter may be separated as much as possible.

Dossie provides a more detailed account of the use of *aurum fulminans* as an artist's material in *The Handmaid to the Arts*, a book first published in 1758, roughly two decades before the *Opuscula* (27). The book, dedicated "to the Noblemen and Gentlemen Members of the Society for the Encouragement of Arts, Manufactures, and Commerce" has been described as "by far the best treatise on the practice of the industrial arts" (28). It consists of three Parts each divided into several chapters, which are in turn subdivided into sections. Chapter IX deals with enamel painting and in Section III of that chapter he deals with the colorants themselves. About the use of *aurum fulminans* he writes (29):

> When a red color is wanted which verges greatly on the purple, a precipitation of the gold should be made by means of any fixt alkaline salt. Which may be thus done.

Dossie then proceeds to outline the same procedure as Valentine and follows it with the remarks:

> The powder thus produced is called *aurum fulminans*, from its quality of exploding when exposed to a moderate heat: which must therefore be carefully guarded against in the use of it, by keeping it out of the reach of any such heat till it be mixed with the flux for enameling.

Thus addition of the flux makes the handling of the material safer, an observation that, as we have already seen, Bergman was able to generalize to all admixed powders.

A reference to the use of *aurum fulminans* in the decorative arts prior to the time of Böttger and Funcke can be found in a little book, *Sol Sine Veste* (*Gold without Vestments*) by Johann Christian Orschall. Very little is known about Orschall's biography (30). He was trained in alchemy and the art of amalgamation (used in the mining of gold and silver) by Johann Heinrich Rudolf in Dresden. In 1684 he was appointed Inspector-General of Mines to Landgrave Carl of Hessen-Kassel because of his promise to greatly improve the yields of the mines at Frankenberg, a task in which he failed and was terminated from his position in 1687. His book was published the year of his appointment, describing the Purple of Cassius one year before the appearance of Cassius' (the younger's) own book, *De Auro* in 1685 (31). Orschall's primary concern in this book was to devise ways to decompose gold into its constituent parts such that it could not be reconstituted, a key step in the quest for transmutation. He describes thirty experiments, two of which are relevant to our topic. As part of experiment 26 Orschall observes (32):

> …I would like to concern myself [with the question] whether the beautiful red comes from gold or whether the salts have something to do with it. What motivates me to raise this question is the gold purple used a lot for painting, which the goldsmiths use to paint glass enamels, the preparation of which is much too well known and not necessary to repeat here, except to remark that it is aurum fulminans…

He then proceeds to recount an explosion he experienced while working with *aurum fulminans* that completely destroyed his expensive jasper mortar and burned him in the face. This somehow brings him to his 27th experiment (33):

> …I have observed this as my 27th experiment, if I want to know whether my gold purple will turn out well I take some of it before it is mixed with flux, hold it to the light [flame] and the stronger and more [loudly] it explodes the more beautiful it will be afterwards…

The sources quoted so far suggest that by the middle of the 17th century goldsmiths were routinely using *aurum fulminans* as a purple colorant in enameling.

Concluding Remarks: Implications for the History of Art

In this paper we have examined the history of a gold compound with, as Bergman wrote, "singular properties" concentrating on its practical use as a colorant in the decorative arts. The evidence assembled from various sources has implication for the history of art, especially the history of early 18th century European porcelain.

Meissen historians have suggested periodically, Lübke as recently as 2004 (34), that *aurum fulminans* is too unstable to be used in ceramics decoration and that the recipe is, somehow, an attempt at misdirection by Höroldt motivated by his penchant for secrecy. This view is fueled in part by the attempts of early 20th century Meissen historians and the Manufactory itself to shroud this technique in secrecy and mystique. The present work should lay to rest any speculation that *aurum fulminans* was actually never used.

More significantly, the documents examined here should elevate the role the goldsmith Funcke played, in the original invention of Böttger luster. Walcha (11) suggests that in his search for usable overglaze colors, Böttger probably sought the advice of goldsmiths who knew how to fire low melting silicate-based colorants on noble metals in a variety of ways. Funcke, a well-established Dresden enameller prior to his association with Böttger was undoubtedly familiar with the use and safe handling of *aurum fulminans*. Enamellers used low melting fluxes unsuitable for porcelain painting, possibly one of the reasons why Böttger could not adopt their formulations for his purposes. The use of inappropriate fluxes may be the cause for the mottled appearance of the decoration on pre-1720 objects. While the fluxes used by Höroldt have been amply described and their composition studied by non-destructive techniques like X-ray fluorescence on numerous occasions, this author is not aware of comparable measurements on objects decorated by Funcke. This essay might hopefully provide the impetus for further research in this area. With the additional insights about how *aurum fulminans* was used in enameling one could also entertain laboratory replication experiments to better understand the details of the procedures used to apply Böttger luster on Meissen porcelain. Replication of historic materials and processes is an increasingly important research tool for a deeper understanding of materials science issues in cultural heritage objects.

Finally while the use of *aurum fulminans* appears to have been discontinued in Meissen after 1735 (35), it persisted considerably longer as a decorative technique in Great Britain. Thus in *The Botanic Garden*, an unusual book published in 1791, combining poetry and technology in an attempt to popularize the science of the day, Erasmus Darwin, grandfather of Charles, wrote (36):

> The fine bright purples or rose colours which we see on china cups, are not producible with any other material except gold; manganese indeed gives a purple, but of a very different kind.
>
> [Darwin goes on to discuss using the Purple of Cassius]…
>
> I am informed that some of our best artists prefer aurum fulminans, mixing it before it has become

dry, with the white composition or enamel flux; when once it is divided by the other matter, it is ground with great safety, and without the least danger of explosion whether moist or dry. The colour is remarkably improved and brought forth by long grinding, which accordingly makes an essential circumstance in the process.

Acknowledgment

We would like to thank the Staatliche Porzellan-Manufaktur Meissen GmbH - Historische Sammlungen for facsimiles of the pages from the Höroldt Recipe book.

Supplemental Material

A color photograph of a Meissen cup and saucer decorated with Böttger luster, courtesy of the Metropolitan Museum of Art, as well as facsimiles of the handwritten pages of Höroldt's recipe and a modern German transcript and English translation by the author, can be found in the Supplemental Material for the *Bulletin for the History of Chemistry* at the journal's website,

www.scs.uiuc.edu/~mainzv/HIST/bulletin/index.php.

References and Notes

1. The process of making porcelain was a closely guarded Chinese trade secret until the reinvention of the basic formulation by Johann Friedrich Böttger, Ehrenfried Walther von Tschirnhaus (1651-1708), and their assistants, the so-called Contubernium, sometime in late 1707 and definitely by the beginning of 1708. Augustus the Strong, Prince Elector of Saxony and King of Poland, signed a decree stating the intention of founding a porcelain manufactory on Jan. 24, 1710. The actual manufactory was founded in the city of Meißen on June 6 of the same year, and is still in operation today. See for example, N. Zumbulyadis, "Böttger's Eureka!: New Insights into the European Reinvention of Porcelain," *Bull. Hist. Chem.*, **2010**, *35*, 24-32.
2. "das guthe weisse Porcellain samt der allerfeinsten Glasur und allem zubehörigen Mahlwerck…" Staatsarchiv Dresden, Loc. 1339, vol. I Johann Friedrich Böttigern und deßen Manufacturen betr., 1707-1719.
3. Zimmermann depicts a pair of beakers with primitive polychrome enameling, one glazed the other unglazed, presented by Böttger to Augustus the Strong in 1710. See E. Zimmermann, *Die Erfindung und Frühzeit des Meissner Porzellans*, Druck und Verlag von Georg Reimer, Berlin, 1908, Figure 70, p 169.
4. The Manufactory Inspector was roughly equivalent to the chief operating officer of a modern day corporation. Similarly, the Manufactory Commission was akin to today's board of directors.
5. Menzhausen, *Johann Melchior Steinbrück Bericht* über *die Porzellanmanufaktur Meissen von den Anfängen bis zum Jahre 1717; Kommentar, Transkription und Glossar*, Edition Leipzig, 1982, p. 228. "…dahero nicht zuzweifeln, man werde das übrige, so noch fehlet, ebenfalls nach und nach finden, und herbÿe bringen. Wie denn vor kurtzen würklich eine neüe Arth von embellissement, so man Perlen Mutter- oder Opal-Glasur nennet, (: ob es wohl keine Glasur ist :) auf das weiße porcelain gebracht worden, so demselben ein neües und sehr schönes Ansehen giebet."
6. J. M. Steinbrück, Meissen Manufactory Archives, Dec. 30, 1719, cited by R. Rückert, "*Biographische Daten der Meißner Manufakturisten des 18. Jahrhunderts*", Bayerisches Nationalmuseum, München, 1990, 146-147. "…Perl-Mutterglasur so auch von Böttgern herrühret, der solche Mehlhorn und Funcke gelehret, und auf seine Kosten (weil sie aus Golde bestehet) experimentiren lassen…"
7. Rückert ref. 6. See also I. Menzhausen, "Das rothe und das weiße Porcellain" in "*Johann Friedrich Böttger; Die Erfindung des europäischen Porzellans*" R. Sonnemann and E. Wächtler, Eds., Büchergilde Gutenberg, 1982, 298-299.
8. Ref. 3 (Zimmermann), Ch. VII, pp 244-271.
9. Ref. 7 (Menzhausen), p 299.
10. Ref. 3 (Zimmermann), p 172.
11. For an account of Höroldt's first year in Meissen see O. Walcha, "Höroldts erstes Arbeitsjahr," *Mitteilungsblatt der Keramikfreunde der Schweiz, Nr. 47*, **1959**, 28-31.
12. R. Seyyfarth, "Johann Gregor Höroldt als Chemiker und Techniker," *Mitteilungsblatt der Keramik Freunde der Schweiz*, **1957**, 22-25.
13. M. Mields, "Die Entwicklung der Aufglasurpalette des europäischen Hartporzellans bis 1731 mit besonderer Berücksichtigung der Arbeiten von Johann Gregorius Höroldt," *Keramische Zeitschrift, Nr. 8*, **1963**, *15*, 453-459.
14. The chapters as listed by Mields (ref. 13) are:
   1. Fluxes
   2. Red pigments
   3. Brown pigments
   4. Black pigments with Manganese
   5. Yellow pigments
   6. Green and bluish-green
   7. Blue (including wet chemistry for the preparation of pure cobalt compounds)
   8. Optical black (as mixture of pigments)
   9. Precipitation of silver
   10. Preparation of the purple color (this procedure is essentially identical to the preparation of the Purple of Cassius and used tin (II) to precipitate nanoparticles of metallic gold which vary from red to purple to blue depending on size).
   11. Mother-of-pearl or copper luster (=Böttger luster)

12. Dissolution and precipitation of gold
13. Japanese yellow
14. Flux for sea-green (Celadon)
15. East Asian (overglaze) blue
16. Old Japanese purple
17. Flux using potash
18. The application of overglaze ground colors
19. Oven and firing of enameled goods
20. Brown highlighting

15. J. M. Stillman, "Basil Valentine: A Seventeenth–Century Hoax," *The Popular Science Monthly*, **1912**, *81,* 591-600. E. O. von Lippmann suggests that chemists in the 17th century already knew that Thölde was the real author of the Valentine corpus, see E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, Vol. 1 Verlag von Julius Springer, Berlin, 1919, 640.
16. L. M. Principe, *The Secrets of Alchemy,* The University of Chicago Press, Chicago and London, 2013, 137-158.
17. B. Valentine, *Last Will and Testament of Basil Valentine, Monke of the Order of St. Bennet*, Edward Brewster, London, 1671, 185-186. The frontispiece points out "Never before Published in English," and "are to be sold at the sign of the *Crane* in St. Pauls Church-yard."
18. G. Agricola, *De Re Metallica*, translated from the first Latin edition of 1556 by H. C. Hoover and L. H. Hoover, New York, Dover Publications, Inc., 1950, 441. On p 354 of the same book the translators indicate that aqua regia was known prior to 1400 AD. According to some scholars the knowledge goes back to the Jabirian Corpus (the writings of the 8th century Islamic alchemist Jabr ibn-Hayyam), while others point to an Italian origin around 1300 AD, see for example, E. O. von Lippmann, *Entstehung und Ausbreitung der Alchemie*, Vol. 1 Verlag von Julius Springer, Berlin, 1919, 487-488.
19. J. Beguin, *Tyrocinium Chymicum E Naturae Fonte et Manuali Experientia Depromptum*, Workshop of Christophorus Glückradt, 1625, 292-295.
20. Ref. 19, p 293. *"Germanicis dicitur das Schlaggoldt Latinis aurum fulminans, id est, quod instar fulminis dissiliendo fragorem acutissimum edit: Crollio vero vocatur aurum volatile."* Beguin here is referring to *Basilica Chymica* by Oswald Kroll (1563-1609), first published in 1608 (see for example p 297 of the 1610 edition).
21. See for example, A. F. Holleman and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter & Co., Berlin, 1964, 476-478.
22. R. Glauber, *De Purgatorio Philosophorum oder von dem Fegefewer der Weisen*, Johan Waesberge, Amsterdam, 1668, 38, (note old German spelling of *Fegefeuer* in the title). Angelus Sala writing in the first half of the 17th century mentions that *aurum fulminans* cannot be prepared if hydrochloric acid is used to make aqua regia instead of ammonium chloride.
23. L. B. Hunt, "Gold based glass and enamel colours," *Endeavour, New Series,* **1981**, *5,* 61-67. Hunt points out that already in 1857 Michael Faraday in his Bakerian Lecture to the Royal Society casually remarked that "I believe the Purple of Cassius to be essentially finely divided gold associated with more or less of oxide of tin." M. Faraday, "Experimental Relations of Gold (and other Metals) to Light," *Phil. Trans. R. Soc. Lond,*, **1857**, *147*, 145-181. It appears that the same conclusion was reached by Pierre Joseph Macquer in his *Dictionnaire de chymie* eighty years earlier as reported by T. P. Hanusa (abstract, HIST 3, 246th ACS National Meeting, Indianapolis, IN, 2013).
24. D. Lübke, "Böttger-Lüster," *Keramos*, **2004**, *185*, 13-22. Lübke reports that fourteen porcelain objects decorated with Böttger luster and dating to 1723-1730 were examined by Alfons Stiegelschmitt of the University of Erlangen using X-ray fluorescence. No tin was detected in any of them.
25. T. Bergman, *Physical and Chemical Essays* (translated by E. Cullen from the original Latin *Opuscula Physica et Chemica*), J. Murray, London, 1784, vol. 2, 134-164.
26. Bergman reports several other noteworthy observations and experimental results that may be of interest to the chemistry historian. In section II he writes "the necessity of employing volatile alkali (i.e. ammonia) in this operation was but little regarded until the present century." He confirms that the precipitate is yellow. Bergman, known for his contributions to the techniques of gravimetric analysis, also reproduces Becher's earlier result that gold calx thoroughly washed and dried exceeds the weight of the gold employed by 1/5 implying a calx to original gold weight ratio of 1.2. This is a remarkably accurate result for the times, when compared to the exact ratio of 1.16 based on the hydrazide structure. In section III he examines the physical and chemical properties of the material, interesting for our purposes is the observation that "When carefully and gradually exploded in a glass phial, it leaves a purple soot." The final section XIV titled "The Phenomenon of Fulmination Explained" (5 pages long) gives a phlogistic interpretation of the phenomenon and should be of interest to scholars of the phlogiston theory.
27. R. Dossie, "*The Handmaid to the Arts*," Nourse, London, 1763.
28. For a detailed, two-part biographical essay on Dossie and his work see F. W. Gibbs, "Robert Dossie (1717-1777) and the Society of Arts," *Ann. Sci.*, **1951**, *7*, 149-172; F. W. Gibbs, "Robert Dossie (1717-1777)," *Ann. Sci.*, **1953**, *9*, 191-193.
29. Ref. 27, p 257.
30. F. W. Strieder, *Grundlagen zu einer Hessischen Gelehrten und Schriftsteller Geschichte* vol. 10, Griesbach Kassel, 1795, 107-110. K. C. Schmieder, *Geschichte der Alchemie*, Verlag der Buchhandlung des Waisenhauses, Halle, 1832, 454.
31. Ref. 23, p 63.
32. J. C. Orschall, *Sol Sine Veste*, Augsburg, 1684, (p 66 of the 1742 edition). "…mich nicht unbillig bekümmern ob dann diese schöne Rothe gewiß und eigentlich vom Gold herrühre oder ob etwan die Salia nicht etwas darbey thun möchten. Dieses nun zu erwegen, bewegt mich das schon zu viel mahlen gemelte Gold⁄⁄ Purpur, damit die

Goldschmiede auf ihr Amulir-Glaß zu mahlen pflegen, dessen Bereitung als zu wohl bekannt, und hier nicht unnöthig zu wiederhohlen, ausser zu melden daß es ein Aurum Fulminans seye,…"

33. Ref. 32, p 68. "… wann ich wissen will ob mein Gold// Purpur schön wird so nehme ich etwas darvon und ehe es mit Fluß versetzet wird halte es in ein Licht und je stärker und mehrer es knallet je schöner es hernacher wird…"
34. Ref. 24. Lübke makes a particularly strong statement on p 14 with the ironic remark that in Meissen, nobody has ever reported regular explosions during porcelain firing, "Nirgends wird überliefert, dass es beim Brennen regelmäßig zu Explosionen kam."
35. The reasons for the discontinuation of Böttger luster have never been spelled out in company documents. The most likely explanation is that this type of decoration fell out of favor with the customers who found opulent gilding more to their taste. So the decision probably reflects rational resource allocation.
36. E. Darwin, *The Botanic Garden*, London, 1791, 184, see Note XXI on Enamels.

About the Author

Dr. Nicholas Zumbulyadis obtained his Diploma in Chemistry in 1971 at the Technical University of Darmstadt, in Germany, and his Ph.D. in Physical Chemistry from Columbia University in 1974. In March 1976 he joined the Eastman Kodak Research Laboratories where he worked as a research scientist until his retirement in June 2005. He is the author of over sixty scientific publications focusing on the application of solid-state nuclear magnetic resonance to problems in materials science. Dr. Zumbulyadis is also a collector of 18th century German porcelain and since his retirement, he is active as an independent scholar in the area of ceramic history. His general research interests include topics at the intersection of the history of chemistry and the history of art. He has written several articles published in art historical journals and has lectured on the subject at major museums and universities. He is currently working on the application of solid-state NMR methods to the characterization and conservation of cultural heritage objects jointly with the Metropolitan Museum of Art, the University of Delaware, and most recently the Rochester Institute of Technology.

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The Society for the History of Alchemy and Chemistry is delighted to announce that the 2014 Partington Prize has been awarded to Evan Hepler-Smith (Princeton University), for his article "'Just as the Structural Formula Does': Names, Diagrams, and the Structure of Organic Chemistry at the 1892 Geneva Nomenclature Congress."

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